Preliminary Study on Preparation of Biodegradable Plastic from Modified Cassava Starch

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Modified cassava starch was prepared from the reaction between starch and maleic anhydride using sodium hydroxide as catalyst and water as solvent. After the reaction finished, the product was neutralized with hydrochloric acid solution. Plastic sheets can be prepared from the modified starch by casting. Preliminary studies on characteristics and some properties of these plastic sheets were done using several techniques. It was found that the amount of maleic anhydride plays an important role in changing the chemical structures of the modified starch and the characteristics of the plastic sheets whereas the reaction time does not affect them. The plastic sheets are fully biodegradable. They are insoluble in typical solvents such as chloroform or in acidic solution at both room and elevated temperatures while they are soluble in hot basic solution. It was also found that modified starch-based plastic sheets have lower glass transition temperatures, lower melting points, higher moisture absorption and higher hardness than unmodified starch-based plastic sheets.

Key words: Biodegradable plastic, modified cassava starch.

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การศึกษาเบื้องต้นในการเตรียมพลาสติกที่ย่อยสลายทางชีวภาพจากแป้งมันสำปะหลังดัดแปร

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แป้งมันสำปะหลังดัดแปรสามารถเตรียมได้จากปฏิกิริยาระหว่างแป้งและมาเลอิกแอนไฮไดรด์ โดยใช้โซเดียมไฮดรอกไซด์เป็นสารเร่งปฏิกิริยาและน้ำเป็นตัวทำละลาย เมื่อสิ้นสุดปฏิกิริยา ทำให้ผลิตภัณฑ์ที่ได้เป็นกลางด้วยการเติมสารละลายกรดไฮโดรคลอริก เมื่อนำแป้งดัดแปรที่เตรียมได้มาขึ้นรูปเป็นแผ่นพลาสติกด้วยวิธีการหล่อและได้ทำการศึกษาลักษณะและสมบัติบางประการของแผ่นพลาสติกดังกล่าวในเบื้องต้นโดยใช้เทคนิคการวิเคราะห์หลายเทคนิค พบว่าปริมาณของมาเลอิกแอนไฮไดรด์ทำให้โครงสร้างทางเคมีของแป้งและลักษณะของแผ่นพลาสติกที่เตรียมได้มีความแตกต่างกัน ในขณะที่เวลาซึ่งใช้ในการทำปฏิกิริยาไม่ส่งผลกระทบใดๆ แผ่นพลาสติกดังกล่าวนี้สามารถย่อยสลายทางชีวภาพได้ทั้งหมด ไม่สามารถละลายในตัวทำละลายทั่วๆไป เช่น คลอโรฟอร์ม หรือสารละลายกรดทั้งที่อุณหภูมิห้องและอุณหภูมิสูง แต่ละลายในสารละลายด่างที่ร้อน นอกจากนี้ยังพบว่าแผ่นพลาสติกซึ่งเตรียมจากแป้งดัดแปรมีสมบัติแตกต่างจากพลาสติกที่เตรียมจากแป้งที่ไม่ได้ดัดแปรกล่าวคือ มีอุณหภูมิกลาสทรานซิชันและจุดหลอมเหลวที่ต่ำกว่า มีการดูดซึมน้ำที่ดีกว่าและมีความแข็งที่สูงกว่า

คำสำคัญ พลาสติกที่ย่อยสลายทางชีวภาพ แป้งมันสำปะหลังดัดแปร

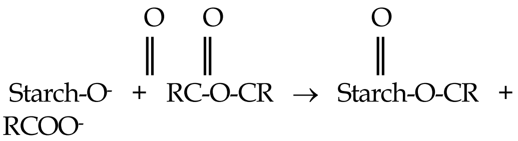
INTRODUCTION

Nowadays, plastic consumption is increasing rapidly. This is because plastics can be used in many applications such as packaging, automobile parts, etc. However, plastics cannot be degraded by natural processes in a short period of time; therefore, they are left as 'plastic waste', causing environmental problems. Methods normally used to destroy other types of waste such as burning and burying are not suitable for plastic destruction. When some types of plastics are burnt, they can release dangerous gases to the atmosphere while burying plastics in soil cannot destroy plastics because they are not biodegradable. Alternative methods to solve this problem have been studied.(1,2) One method that has been developed is to replace commonly used plastics prepared from synthetic polymers with biodegradable plastics prepared from natural polymers.

A widely used natural polymer is starch because it is abundant and inexpensive. Since its molecules are closely packed due to its structural regularity and tightly bonded by hydrogen bonds, its melting point is above its decomposition temperature.(3) This causes difficulty in preparation of plastic directly from starch. Besides, many properties of the resulting plastic are not suitable for many applications in which synthetic polymers are normally used.(3-5) Consequently, most of the research has been concentrated on blending or copolymerizing starch with synthetic polymers.(3-5)

However, the plastics obtained from these methods are only partially biodegradable.(6) Therefore, the preparation of fully biodegradable starch-based plastics was studied. It was found that chemically modified starches can be used as precursors to prepare the desired plastics. The successful modification method for starch is to use acid chlorides or anhydrides as modifying agents in aprotic solvents such as DMSO and with catalysts such as pyridine.(6-8) Although this method is effective, the chemicals are expensive and dangerous. Therefore, a simpler and cheaper method for modifying starch based on the following reactions(7,9) was attempted in this research. Furthermore, preliminary studies on the possibility to form plastic from the modified starch and some properties of the obtained plastic were investigated.

$$\text{Starch-OH} + \text{OH}^- \rightarrow \text{Starch-O}^- + \text{H}_2\text{O}$$



$$\text{Starch-O}^- + \text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R} \rightarrow \text{Starch-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R} + \text{RCOO}^-$$

MATERIALS AND METHODS

Materials

Cassava starch was obtained from Thai Wah Co., Ltd. Maleic anhydride (MA), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol, methanol, toluene, chloroform, xylene, acetone, sulfuric acid, tetrahydrofuran (THF), and petroleum ether were obtained from Fluka and Aldrich Companies. All materials were used as obtained without further purification.

Methods

1. Modification of Cassava Starch

Cassava starch was dried in a vacuum oven at 80°C overnight and it was left to cool down in a desiccator. The dried starch (15 wt % of water) was slowly added into a beaker containing aq. NaOH solution at 50°C (NaOH:MA = 2.2:1 in molar proportion). After the mixture was homogenous, MA* was slowly added to the mixture. The reaction time was maintained as desired**. After that, the product was neutralized by aq. HCl solution.

* The amounts of MA used were 25%, 50% and 75% of MA acidic groups in molar proportion to hydroxyl groups of starch.

** The reaction times used were 2, 4 and 6 hours.

2 . *Characterization of Modified Starch*

Two portions were taken from the modified starch mixture. One portion was poured into ethanol. The precipitate was recovered, washed with ethanol and dried in a vacuum oven. The other portion was dried in a vacuum oven without precipitation from ethanol. Both portions were then characterized by FT-IR spectroscopy using an FT-IR Spectrometer Model Nicolet-Impact 400.

3. *Preparation of Sheet Samples from Modified Starch by Casting*

The modified starch mixtures obtained from 1 were poured into plastic molds. The samples were left to dry at room temperature. After drying, the samples were soaked in 75% ethanol for 10 minutes and then they were left to dry at room temperature. Sheet samples were obtained.

4. *Solubility Test*

The sheet samples were cut into small pieces of 0.5 g. They were put into 10 ml test tubes containing 3 ml of a solvent. The solubility of the samples was observed at both room and elevated temperatures.

5. *Moisture Absorption*

The samples with a size of 1 x 1 x 0.3 cm were dried in a desiccator until their weights became constant (W_0). These samples were then placed in normal atmosphere for 24 hours. After that, the samples were weighed (W_1). % moisture absorption, (%M) can be calculated from the following equation:

$$\%M = (W_1-W_0)/W_0 \times 100$$

6. *Thermal Analysis*

Thermal properties of the sheet samples were studied by differential scanning calorimetry (DSC) using differential scanning calorimeter Mettler Toledo Model 822e with a temperature range of 25-200°C and a heating rate of 10 °C/min.

7. *Hardness Test*

Hardness of the samples was determined according to ASTM D 2240.(10)

8. *Biodegradability Test*

Biodegradability test was done based on the soil burial method.(6) Samples with a size of 5 x 1 x 0.3 cm were dried in desiccator until their weights became constant (W_2). These samples were then buried in soil for 1 month. After that, the samples were dried in a desiccator until their weights became constant (W_3). % weight loss, (%W) can be calculated from the following equation:

$$\%W = (W_2 - W_3)/W_2 \times 100$$

RESULTS AND DISCUSSION

All modified starch mixtures obtained after neutralization with HCl solution were slightly viscous liquids. The color of the mixtures prepared with MA 75% at every reaction time was slightly yellow whereas the color of mixtures prepared with MA 25% and 50% at every reaction time was creamy white.

The FT-IR spectroscopic results (Figure 1) indicate that the amount of MA has a significant effect on the chemical structures of the modified starches. The broad peak at a wavenumber range of 3200-3600 cm^{-1} corresponds to OH stretching. It can be seen that as the amount of MA increases, this peak spilt into two peaks. This indicates two types of OH stretching which are from OH groups and COOH groups. All modified starches show broad peaks at a wavenumber range of 1560–1610 cm^{-1} which corresponds to COO of ester groups. The intensity of this peak increases with increasing amounts of MA. However, it is clearly seen in the FT-IR spectrum of modified starch with MA 75 % that this broad peak actually splits. This indicates the presence of $COO^- Na^+$. The peaks at wavenumber around 870 cm^{-1} in the FT-IR spectra of the modified starches indicate the presence of carbon-carbon double bonds (C=C). The FT-IR spectra of the purified modified starches prepared with the reaction times of 4 and 6 hours also showed the same results. On the other hand, FT-IR spectra of modified starches prepared with different reaction times using MA 25 % shown in Figure 2 are similar. The FT-IR spectra of modified starches prepared with MA 50 % and 75 % also showed the same results. These results suggest that the reaction time has no effect on the chemical structures of the modified starches and the reaction time of 2 hours may be enough to complete the modification reaction.

Figure 1. FT-IR spectra of unmodified and modified starches with 25%, 50% and 75% of MA using reaction time of 2 hours.

Actually, when the anion of starch reacts with MA, the sodium salt of starch is obtained. After neutralization, purification and drying, the acid product should be obtained. However, the results of FT-IR spectroscopic analysis suggest that the modified starch is composed of 2 structures as follows:

Starch-O-CO-CH=CH-COOH

and

Starch-O-CO-CH=CH-COO^- Na^+

This indicates that there were some salt groups which were not neutralized.

Figure 2. FT-IR spectra of modified starches with 25% of MA using reaction times of 2, 4 and 6 hours.

When the FT-IR spectra of unpurified and purified modified starches were compared, it was found that they are similar. This suggests that there is no unreacted MA in unpurified modified starch so the obtained modified starch mixtures after neutralization from 1 were directly used to prepare sheet samples without precipitation from ethanol. Since these mixtures are already in liquid form, it is easy to pour them into molds. However, NaCl, a by-product from the modification, will remain in the samples. Although it is not dangerous, it may affect the samples' properties. It was removed by soaking the sheet samples obtained from casting in 75% ethanol for 10 minutes and then drying. Table 1 gives the characteristics of the sheet samples before and after NaCl removal. The sample number abbreviation indicates the amount of MA used and the reaction time such as SMS-25-2 which means sheet sample cast from modified starch mixture prepared with MA 25% using a reaction time of 2 hours. It can be seen that the more NaCl left, the more translucent the samples. The amount of NaCl depends on the amount of HCl solution used in neutralization which corresponds to the amounts of NaOH and MA used in modification. After the NaCl was removed, the samples became colorless and transparent.

From Table 1, it can be seen that the characteristics of the sheet samples can be divided into 3 groups, depending on the amount of MA. In the case of flexibility, the factor which affects this property is the carbon-carbon double bond of MA. Since the double bond is a stiff segment, it reduces the flexibility of the chain; therefore, the less number of double bonds, the greater flexibility of the sample. An increase in toughness of the samples with decreasing the amount of MA is due to the fact that the MA segment increases the distance between starch molecules; consequently, fewer hydrogen bonds are formed. Therefore, when force is applied, the samples with fewer hydrogen bonds are easier to split.

Furthermore, it was found that the sheet samples cast from modified starch mixtures prepared with the same amount of MA but different reaction times have the same characteristics. This also demonstrates that the reaction time has no effect on the chemical structure of the modified starches.

Since the reaction time has no effect on the chemical structures of the modified starch, this suggests that a reaction time of 2 hours should be used if this process is applied in industry. Therefore, some further properties of sheet samples prepared using a reaction time of 2 hours were studied.

Table 1. Characteristics of sheet samples before and after NaCl removal.

Sample No.	Before NaCl Removal	After NaCl Removal
SMS-25-2 SMS-25-4 SMS-25-6	colorless, transparent, flexible, tough and difficult to split	colorless, transparent, flexible, tough and difficult to split
SMS-50-2 SMS-50-4 SMS-50-6	white, translucent, less flexible than SMS-25, not tough and easy to split	colorless, transparent, less flexible than SMS-25, not tough and easy to split
SMS-75-2 SMS-75-4 SMS-75-6	white, more translucent than SMS-50, less flexible than SMS-50, not tough and very easy to split	colorless, transparent, less flexible than SMS-50, not tough and very easy to split

Table 2. Properties of sheet samples prepared with different amount of MA using a reaction time of 2 hours.

Properties	%MA in Modification			
	0	25	50	75
T_g (°C)	155	90	75	50
T_m (°C)	*	154	138	135
Moisture Absorption (%)	3.3	10.5	15.7	17.7
% weight loss in 1 month	97.8	98.5	100	100
Hardness shore D	46	54	57	60

* T_m of unmodified starch was not observed because it is above the decomposition temperature.

It is clearly seen that when the amounts of MA used in modification increase, the glass transition temperatures (T_g) and the melting temperatures (T_m) decrease. This may be because the MA segments increase the distance between the starch molecules and this results in less packing and less hydrogen bonding. Consequently, it is easier for starch molecules to rotate or move when they are heated. Since starch molecules are less-packed, it is easy for the sheet samples to absorb moisture from the atmosphere and it is easy for microorganisms in the soil to penetrate the sheet samples. Therefore, % moisture absorption and % weight loss increase when the amounts of MA used in modification increase. The % weight loss also indicates that the plastic prepared from modified cassava starch is fully biodegradable.

From Table 2, it can be seen that the hardness of unmodified starch is less than those of modified starches. The hardness of modified starches shows a tendency to increase with increasing the amounts of MA in modification. This is a result of an increase in stiffness of the molecule due to the carbon-carbon double bond.

Table 3. Results of solubility tests of sheet samples prepared with different amounts of MA using reaction time of 2 hours.

Solvent	% MA in Modification					
	25		50		75	
	T_r	T_e	T_r	T_e	T_r	T_e
Acetone	×	×	×	×	×	×
Chloroform	×	×	×	×	×	×
Ethanol	×	×	×	×	×	×
Methanol	×	×	×	×	×	×
Petroleum Ether	×	×	×	×	×	×
THF	×	×	×	×	×	×
Toluene	×	×	×	×	×	×
Xylene	×	×	×	×	×	×
10 % H_2SO_4 Solution	s	s	s	s	s	s
10 % NaOH Solution	s√	√	s√	√	s√	√
Water	s	√	s	√	s	√

T_r = room temperature

T_e = elevated temperature = 60 °C for 1 hour

√ = soluble

× = insoluble

s = swell

s√ = some part is soluble and some part swells

Table 3 shows the results of solubility tests. It can be seen that the samples are not soluble and do not swell in common solvents such as chloroform, acetone, and THF, even at elevated temperatures. Acidic solutions and pure water can make the samples swell but water can dissolve the samples at elevated temperature. For basic solution at room temperature, some parts of the samples are soluble while the remaining parts swell. At elevated temperatures, all parts of the samples completely dissolve.

It can be suggested that this method is suitable for industrial applications because all the reactants used in modification are cheap and easy to find. Furthermore, both the modification process and plastic formation process (casting) are simple and practical.

CONCLUSION

Cassava starch can be modified by using maleic anhydride as modifier, sodium hydroxide as catalyst and water as solvent at 50 °C. The plastic sheets can be formed from the modified starches by casting. When the amount of maleic anhydride used for modification increases, the difference between the chemical structures of unmodified and modified starches increases. The flexibility of the plastic sheets increases and the toughness of the plastic sheets decreases with increasing the amount of maleic anhydride. However, the reaction time does not affect either the chemical structures of the modified starches or the characteristics of the resulting plastic sheets. The results suggest that a reaction time of 2 hours is suitable for the modification process. It was found that plastic sheets are fully biodegradable. They are insoluble in typical solvents and acidic solution at both room and elevated temperatures. They are, however, soluble in hot basic solution. The plastic sheets prepared from modified starch have lower T_gs and T_ms, higher hardness and higher % moisture absorption than that prepared from unmodified starch.

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